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<b>(21) International Application Number:</b> PCT/US94/03164 <b>(22) International Filing Date:</b> 23 March 1994 (23.03.94) <b>(30) Priority Data:</b> 93201007.7 6 April 1993 (06.04.93) EP <i>(34) Countries for which the regional or international application was filed:</i> BE et al. <b>(71) Applicant (for all designated States except US):</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> SCIALLA, Stefano [IT/IT]; Viale dei Caduti nella Guerra di Liberazione, 131, I-00128 Roma (IT). <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45202 (US).		<b>(81) Designated States:</b> AU, CA, CZ, JP, PL, RU, US.  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> LAVATORY BLOCKS CONTAINING ENZYMES  <b>(57) Abstract</b>  A solid lavatory block comprising an enzyme system. Said lavatory blocks are environmentally compatible and provide enhanced stain removal.		

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## LAVATORY BLOCKS CONTAINING ENZYMES

### Field of the Invention

The present invention relates to solid lavatory cleansing blocks containing enzymes. The block is designed to have good stain removal capacity.

### Background of the Invention

Lavatory blocks for cleansing and deodourizing the lavatory bowl are well known in the art. Such lavatory blocks typically comprise surfactants and chlorinating compounds which provide the desired cleansing and deodourizing properties.

However, the lavatory blocks disclosed in the prior art do not efficiently address the problem of stain removal of

physiological soils which are frequently found in the lavatory bowl. The surfactants contained in the lavatory blocks on the market are not present in sufficiently high concentrations in order to achieve optimum improved stain removal. Chlorinating agents due to their bleaching action are known for their stain removal ability. The in-bowl stain removal action of said chlorinating agents is limited at low concentrations.

It is therefore an object of the present invention to provide an efficient stain and grease removal system incorporated in a solid lavatory block which is completely environmentally safe.

In response to these objectives, the present invention proposes to formulate a lavatory block comprising an enzyme system as a stain removal active.

The blocks according to the present invention progressively dissolve in water, thereby releasing the ingredients in solution. Thus, a permanent aqueous solution is provided in the lavatory bowl which comprises a constant and predetermined amount of various ingredients.

An advantage of the present invention is that the enzymes are permanently active in the lavatory bowl water during the whole period in between lavatory flushes.

#### Summary of the Invention

The present invention is a solid lavatory block characterized in that it comprises from 0.1% to 50% of an enzyme system, whereby said lavatory block provides a permanent aqueous solution comprising an effective amount of said enzyme system as said block is progressively dissolved in said lavatory bowl water.

All ratios, percentages and parts given herein are "by weight" unless otherwise specified.

Detailed Description of the Invention

The present invention relates to a solid lavatory cleansing block. There are two types of lavatory blocks available on the market at present, in-rim and in-cistern type lavatory blocks. The in-rim type blocks are distinct from in-cistern type blocks in that they are designed to be hung from the rim of the lavatory bowl, in a conventional type rim cage. The in-cistern type blocks are designed to be placed in the cistern itself. Depending on the positioning of the block the properties of the active ingredients will vary, depending on the length of time the block is immersed in water. The lavatory blocks according to the present invention are designed to be used as both in-rim and in-cistern type lavatory blocks.

The blocks according to the present invention progressively dissolve in water, thereby releasing the ingredients in solution. Thus, a permanent aqueous solution is provided in the lavatory bowl which comprises a constant and predetermined amount of various ingredients.

The lavatory blocks of the present invention comprise as an essential feature from 0.1% to 50%, preferably from 1% to 40%, more preferably from 2% to 25% of an enzyme system. Suitable enzymes which may be used are selected from lipases, proteases, cellulases, amylases, polysaccharide hydrolases and mixtures thereof. The preferred enzyme for use herein is lipase.

Typically lavatory blocks according to the present invention comprise a lipase enzyme such that the lipolytic activity of the lavatory block is from 0.01 to 5000 KLU, preferably from 0.1 to 1000 KLU, most preferably from 1 to 150 KLU per gram of the lavatory block. KLU are standard kilo units defined by Novo for measuring lipase activity.

The lavatory blocks according to the present invention typically comprise a protease enzyme such that the protolytic activity of the lavatory block is from 0.01 to 500 KNPU,

preferably from 0.05 to 200 KNPU, most preferably from 1 to 100 KNPU per gram of the lavatory block. KNPU denotes Kilo Novo Protease Units.

The lavatory blocks according to the present invention typically comprise an amylase enzyme such that the amylolytic activity of the lavatory block is from 0.01 to 500 KNU, preferably from 0.1 to 250, most preferably from 1 to 100 KNPU per gram of the lavatory block. KNU are Kilo Novo units used for measuring amylase activity.

Typically, lavatory blocks according to the present invention comprise a cellulase enzyme such that the cellulytic activity of the lavatory block is from 0.01 to 50 000 CEVU, preferably from 0.1 to 10 000 CEVU, more preferably from 1 to 1500 CEVU per gram of the lavatory block. CEVU are standard units for measuring cellulase activity.

Commercially available enzymes for use herein include :

- protease of Bacillus, especially from B. licheniformis (e.g. Alcalase(R) and from alkalophilic Bacillus strains according to US 3 723 250 (e.g. Savinase(R)) (both available from Novo Industri A/S).
- Alpha-amylase of Bacillus, especially B. licheniformis, Termamyl(R) (Novo Industri A/S).
- Protease of Fusarium, especially F. oxysporum, US 3 652 399 (Takeda), PCT/DK 89/00001.
- Cellulase of Humicola, especially H. Insolens. Celluzyme(R). (Novo Industri A/S), US 4 435 307 (Novo).
- Lipase of Humicola, especially H. lanuginosa, Lipolase(R) (Novo), EP 305 216 (Novo) and US 4 810 414 (Novo).

The enzyme system assists in the removal of faecal, urine and grease stains which are found in the lavatory bowl. It is believed that enzymes, especially lipases are effective in removing the stains found in the lavatory bowl by attacking the components present in faeces which represent a significant fraction of the faecal soil.

The lavatory blocks according to the present invention may also contain a number of optional ingredients. One such ingredient is a surfactant system. The incorporation of a surfactant provides increased cleansing of the lavatory blocks and provides a solid matrix in which all the other ingredients can be incorporated. The block comprises at least 10% of a surfactant system. The surfactants that may be used herein can be anionic and nonionic surfactants or mixtures thereof.

The anionic surfactants which may be used in the present invention include for example alkali metal salts of alkyl substituted benzene sulphonates, alkali metal alkyl sulphonates, alkali metal alkyl sulphates and alkali metal alkyl ether sulphates derived for example from fatty alcohols and alkyl phenols, alkali metal alkane sulphonates, alkali metal olefin sulphonates and alkali metal sulphosuccinates, whereby the sodium salts are preferred. Most preferred are sodium alkyl metal sulphonates and sulphates.

The nonionic surfactants which may be used can be chosen from any liquid or solid ethoxylated C<sub>6</sub>-C<sub>24</sub> fatty alcohol nonionic surfactant, fatty acid C<sub>6</sub>-C<sub>24</sub> alkanolamides, C<sub>6</sub>-C<sub>20</sub> polyethylglycol ethers, polyethyleneglycol with molecular weight 1000 to 80000 and C<sub>6</sub>-C<sub>24</sub> amine oxides.

The lavatory blocks of the present invention may further comprise from 0.001% to 10%, preferably from 0.001% to 3% soluble calcium salts. The calcium salts can be used to stabilize the enzymes.

The lavatory blocks of the invention may further comprise 0% to 50%, preferably from 5% to 30%, fillers of inorganic salts such as sodium sulphate, sodium carbonate, sodium silicate and less preferably phosphorous sodium salts, for example sodium triphosphate, or inert fillers such as clay, urea or calcite. The fillers can be used to adjust the mechanistic properties of the lavatory blocks so that the active ingredients are released in the desired manner.

The differences in the composition of the in-rim and in-cistern type lavatory blocks of the present invention can be exclusively but not necessarily dependant upon the type of surfactants, fillers and polymers used therein, to determine the dissolution rate. The composition differences are well known in the art. In-cistern type lavatory blocks can preferably contain surfactants with a lower solubilization rate and may be chosen from long chain higher anionics or nonionics with a high degree of ethoxylation. In-cistern type lavatory blocks may also contain specific ingredients to decrease the solubilization rate such as slowly dissolving polymers or oils.

The lavatory blocks of the present invention may further comprise as an optional feature from 1ppm to 500ppm, preferably from 5ppm to 300ppm, more preferably from 10ppm to 200ppm active oxygen in the lavatory bowl water. The source of active oxygen can be selected from hydrogen peroxide or sources thereof, preformed peroxyacids, organic peroxides and mixtures thereof. As used herein active oxygen concentration refers to the percentage concentration of elemental oxygen, with an oxidation number zero, that being reduced to water would be stoichiometrically equivalent to a given percentage concentration of a given peroxide compound, when the peroxide functionality of the peroxide compound is completely reduced to oxides.

A hydrogen peroxide source according to the present invention refers to any compound which produces hydrogen peroxide when said compound is in contact with water. Suitable water-soluble sources of hydrogen peroxide for use herein include persulfates, percarbonates, metal oxides and perborates.

Suitable preformed peroxyacids for use in the lavatory blocks according to the present invention include diperoxydodecandioic acid DPDA, magnesium perphthalate, perlauric acid, perbenzoic acid, diperoxyazelaic acid and mixtures thereof. The blocks according to the present invention comprise from 0.01% to 30% of said preformed peroxyacids.



Suitable organic peroxides for use in the lavatory blocks according to the present invention include diacyl and dialkyl peroxides such as dibenzoyl peroxide, dilauroyl peroxide, dicumyl peroxide and mixtures thereof. The blocks according to the present invention comprise from 0.01% to 30% of said organic peroxides.

Optionally, the lavatory blocks may additionally comprise peracid precursors, i.e. compounds that upon reaction with hydrogen peroxide produce peroxyacids. Examples of peracid precursors suitable for use in the present invention can be found among the classes of esters, amides, imides and anhydrides such as acetyl triethyl citrate (ATC), tetra acetyl ethylene diamine (TAED), succinic or maleic anhydrides. All of these bleaching agents are environmentally compatible and odourless.

Another optional component of said system is an acid or alkali. The acid or alkali is used to ensure that the pH of the lavatory bowl water is in the range of pH 4 to pH 10. The stability and activity of the enzymes of the present invention can be optimized by ensuring that the pH of said lavatory bowl water is at the optimum level for the enzyme used herein.

The acids of the present invention that may be used for this purpose may in addition have the advantage that they can form small concentrations of the corresponding peracids by reaction with hydrogen peroxide in-situ, thus enhancing the overall performance of the lavatory block. These acids can be further selected so as to have chelating and/or building properties, which results in limescale removal. The acids that can be used in the present invention are organic or inorganic acids, preferably organic acids such as citric, maleic, oxalic succinic and tartaric acids, more preferably citric and maleic acids.

The alkalis that may be used in the present invention include sodium hydroxide, potassium hydroxide, alkali metal hydroxides,

alkaline earth metal hydroxides and amines, for example monoethylamine, monoethanolamine and triethanolamine.

Another additional ingredient of the lavatory block is a chelant system. The chelant system improves the overall limescale/rust removal performance. Furthermore, the chelant system may improve the stability of the bleaching agent in the formulation. Suitable chelants may be chosen from EDTA, NTA or preferably from biodegradable chelants such as s,s-ethylene diamino disuccinate and dipicolinic acid.

Further optional ingredients include perfumes and dyes used to improve the aesthetics of the lavatory block. These perfumes and dyes contained in the lavatory block are selected for their stability in the presence of the source of active oxygen. In a preferred embodiment of the present invention, where said blocks comprise perfumes and dyes, it is desirable to manufacture said blocks in a process whereby said perfumes and dyes can be premixed with the enzymes and the other optional ingredients, before the addition of the source of active oxygen if said compound is a component of the lavatory block.

The lavatory cleansing block is formed by conventional methods well known in the art as described for instance in EP-A 462 643. The ingredients are mixed to form a dough of suitable consistency which can then be extruded and cut into lengths to form blocks. The extrusion process can be carried out by using simple conventional extrusion equipment such as usually used for manufacturing soap bars. Alternatively, the lavatory blocks may be prepared by compressing all of the ingredients into a block.

The present invention is further illustrated by the following examples.

Examples

The following compositions are made by combining the listed ingredients, in the listed proportions.

<b>EXAMPLES No. 1,2,3,4</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Ingredients	Weight	%		
Sodium Coconut Alkyl Sulphate	50	53	55	55
Lutensol A030	5	2	-	-
Sodium Sulphate	30	30	28	28
Lipolase <sup>R</sup> 100L	10	5	5	5
Savinase <sup>R</sup> 8.0L	-	5	5	3
Celluzyme <sup>R</sup>	-	-	2	2
Perfume	4	4	4	4
Dyes or pigments, water	Balance	Balance	Balance	Balance

<b>EXAMPLES No. 5,6,7,8</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>
Ingredients	Weight	%		
Sodium Coconut Alkyl Sulphate	50	50	50	55
Lauryl Ether Sulphate	3	3	3	-
Sodium Sulphate	10	10	13	15
Lipolase <sup>R</sup> 100L	5	5	5	5
Savinase <sup>R</sup> 8.0L	3	3	3	-
Sodium Persulphate	-	10	10	8
Citric Acid	20	10	10	10
Dipicolinic Acid	3	3	3	-
Perfumes	5	5	5	6
Dyes or pigments, water	Balance	Balance	Balance	Balance

**CLAIMS**

1. A lavatory cleansing block **characterized in** that it comprises from 0.1% to 50% of an enzyme system, whereby said block provides a permanent aqueous solution comprising an effective amount of said enzyme system as it dissolved in the lavatory bowl water.
2. A lavatory cleansing block according to claim 1, wherein said enzyme system comprises enzymes selected from lipases, cellulases, proteases and amylases or mixtures thereof.
3. A lavatory cleansing block according to claim 2, wherein said enzyme is a lipase.
4. A lavatory cleansing block according to claims 1 to 3, wherein said permanent aqueous solution has a pH from 4 to 10.
5. A lavatory cleansing block according to claims 1 to 4, further comprising above 10% of a surfactant system.
6. A lavatory cleansing block according to claims 1 to 5, further comprising from 1ppm to 500ppm of active oxygen as said block is progressively dissolved in said lavatory bowl water.
7. A lavatory cleansing block according to claim 6, wherein said source of active oxygen is selected from hydrogen peroxide or a source thereof, preformed peroxyacids, peroxides and mixtures thereof.
8. A lavatory cleansing block according to claims 1 to 7, further comprising from 0% to 20% of a chelant system.
9. A lavatory cleansing block according to claims 1 to 8, further comprising from 0% to 50% of a filler system.

10. A lavatory cleansing block according to claims 1 to 9, further comprising from 0% to 20% of an peracid precursor.

11. The use of an enzyme system in a lavatory cleansing block to remove stains in the lavatory bowl.

## INTERNATIONAL SEARCH REPORT

 International application No.  
 PCT/US94/03164

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C11D 3/386

US CL : 252/174.12, 174, DIG. 12, DIG. 16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/174.12, 174, DIG. 12, DIG. 16

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US, A, 4,842,762 (SABOL, JR. ET AL) 27 JUNE 1989, SEE EXAMPLES 1-4; SEE COL. 8, LINES 51-52.	1-2 ----- 3
A	US, A, 5,178,787 (HUNG ET AL) 12 JANUARY 1993, SEE ENTIRE DOCUMENT.	1-3
X ---- Y	US, A, 3,798,181 (VAZQUEZ) 19 MARCH 1974, SEE COL. 6, LINES 23-24; EXAMPLES 1.	1-2 ----- 3
A	US, A, 4,248,827 (KITKO) 03 FEBRUARY 1981, SEE ENTIRE DOCUMENT.	1-3
X ---- Y	EP, A, 0,466,484 (FRY) 15 JANUARY 1992, SEE COL. 7, LINES 54-55; SEE COL. 3, LINE 17- LINE 45.	1-2 ----- 3

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search

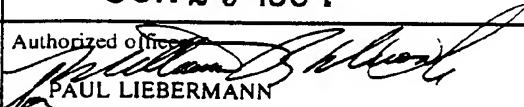
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**INTERNATIONAL SEARCH REPORT**

International application No.  
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO, A, 89/12090 (VAN DIJK) 14 DECEMBER 1989, SEE COL. 4, LINES 25-26; COL. 2, LINE 1-27.	1-3

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/03164

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☒ Claims Nos.: 11  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  
  
THE WORDING OF THE CLAIM "USE OF" IS CONSIDERED VAGUE IN THAT THE OFFICE IS NOT SURE WHETHER SUCH CLAIM IS A METHOD OF USE OR A COMPOSITION.
  
3. ☒ Claims Nos.: 4-10  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.